

# Impedance Studies Of Proton Conducting Plasticized Polymer Electrolyte Based On Starch

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## Abstract

In the present work, plasticized polymer electrolytes based on starch has been prepared by solution casting technique. The conductivity of the films has been characterized using impedance spectroscopy at various frequencies and temperatures. The impedance plot for the films containing 4 wt. % of glycine consists of a spike at the low frequency end of the plot and the conductivity obtained at room temperature was  $(8.55 \pm 0.89) \times 10^{-5} \text{ S cm}^{-1}$ . The temperature-dependent conductivity data obeys Arrhenius relationship. The dielectric constant increased with the increase in temperature and decreased with the increase in frequency.

**Keywords:** starch,  $\text{NH}_4\text{NO}_3$ , glycine, impedance, conductivity

## 1. INTRODUCTION

Since Wright [1] discovered ionic conduction in PEO complexes, a lot of development on many polymeric materials that support ionic conduction can be observed. Studies of the electrical properties of polymeric materials are important because quantities that include ionic conductivity, dielectric properties and conduction mechanism can be determined from such studies. Ideally, the ionic conductivity for an electrolyte system particularly for electrochemical devices should be in the range between  $10^{-4}$  to  $10^{-1} \text{ S cm}^{-1}$ . One powerful technique that has been used to investigate the electrical properties of electrode and electrolyte materials for solid-state electrochemical devices is the complex impedance spectroscopy (CIS) [2]. By using complex impedance spectroscopy, Cole-Cole plots can be constructed and thus determines the bulk resistance,  $R_b$  of the polymer. Using this bulk resistance, frequency dependent conductivity could be evaluated to characterize the polymer [3]. A number of

study have attempted to develop and characterize SPEs from polymer including poly(ethylene oxide) (PEO), poly (vinyl alcohol) (PVA) and strong acids [4]. However due to current situation, materials from natural and renewable resources including starch have attracted attention of many researchers due to their good mechanical and electrical properties [5].

This present work looks at the conductivity and dielectric properties of a glycine-plasticized starch based polymer electrolyte system that has been experimentally obtained using impedance data.

## 2. EXPERIMENTAL

Impedance spectroscopy was performed using a HIOKI 3522-01 LCR Hi-Tester interfaced to a computer with frequency range of 50 Hz to 1 MHz to study the ionic conductivity of the samples. The conductivity was also studied in the temperature range between 303 and 373 K. The film was sandwiched between two blocking stainless steel electrodes of a conductivity cell. The ionic conductivity of



the sample was calculated from the equation below

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where  $A$  is the area of the film-electrode contact,  $t$  is the thickness of the film and  $R_b$  is the bulk resistance of the film in ohms obtained from the complex impedance measurements.

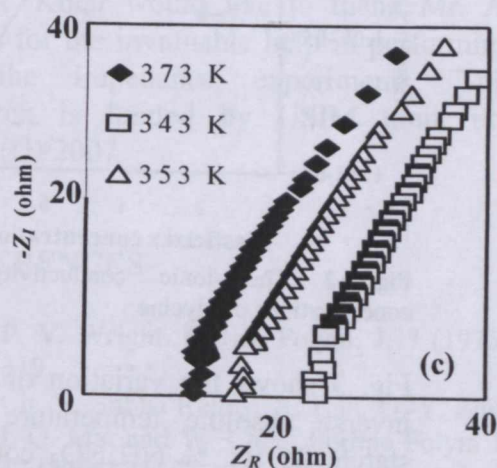
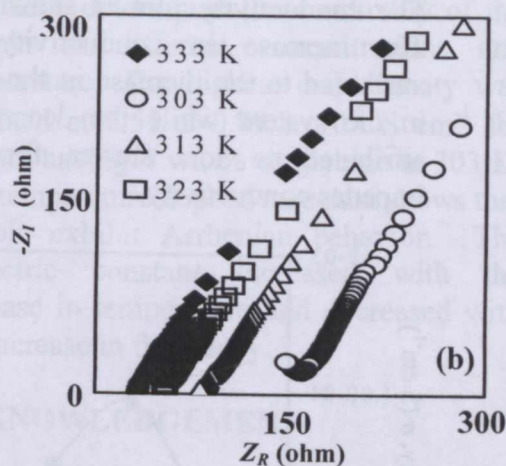
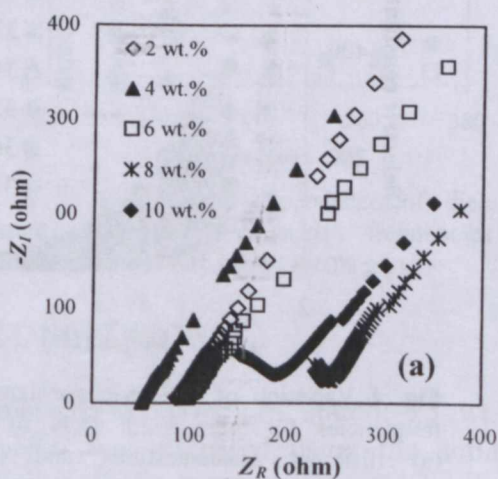
### 3. RESULTS AND DISCUSSION

Complex impedance is given by

$$Z = Z' - jZ'' \quad (2)$$

$$Z = \frac{D}{\omega C} - \frac{j}{\omega C} \quad (3)$$

where  $Z'$  is the real part of impedance;  $Z''$  imaginary part of impedance;  $D$  = loss tangent;  $\omega$  = angular frequency;  $C$  = capacitance of the film. Fig. 1(a) shows the typical Cole-Cole plot for (starch: 25 wt. %  $\text{NH}_4\text{NO}_3$ ) polymer electrolyte at different concentrations of glycine and different temperature, respectively. It is observed that the semicircle occurs at higher frequency only for higher plasticizer concentrations (8-10 wt. %) whereas at lower concentrations (2-6 wt. %), the plots show an inclined straight line which is due to the effect of blocking electrode [6].



**Fig. 1** The impedance plot for starch + 25 wt.% of  $\text{NH}_4\text{NO}_3$  at (a) different glycine concentrations and at different temperatures of (b) 303-333 K and (c) 343-373 K

The disappearance of the semicircle suggests that only the resistive component of the polymer prevails owing to the mobile ions in the polymer matrix. The inclination of the spike at an angle less than  $90^\circ$  shows that there is non-homogeneity between the electrolyte and the electrode [6]. In Fig. 1(a), the sample with 4 wt. % of glycine also have the smallest  $R_b$  which implies that it has the highest conductivity. Fig. 1(b) shows the impedance plot for the highest conducting sample at different temperatures. It has been found that the bulk resistance decreases as the temperature increases which in turn leads to the increase in the conductivity of the system.



The conductivity plot is shown in Fig. 2. The increase in conductivity could be attributed to the increase in the mobile ions in the system while the decrease may be attributed to ion cluster formation that impedes conductivity.

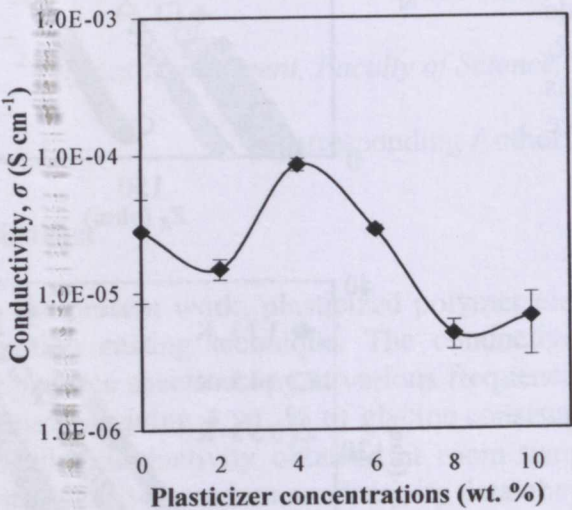


Fig. 2 The ionic conductivity at various concentrations of glycine

Fig. 3 shows the variation of  $\log(\sigma)$  with inverse absolute temperature for various starch: 25 wt. %  $\text{NH}_4\text{NO}_3$  complexes. The linear variation of this plot suggests an Arrhenius-type thermal activated process has occurred. Linear relations are observed in all characterized polymer electrolytes, indicating that there is no phase transition in the polymer matrix or domain formed by addition of glycine. Table 1 lists the conductivity value and activation energy for each sample.

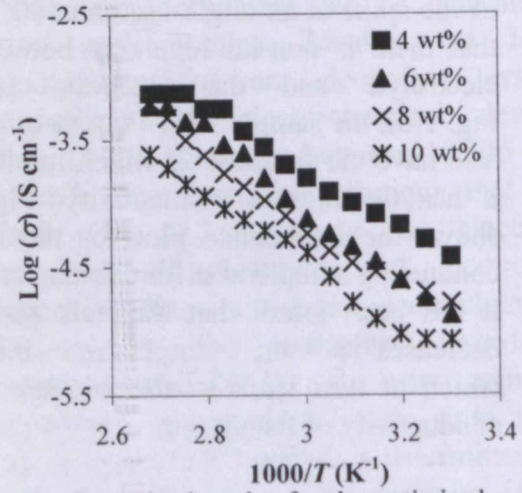


Fig. 3 Arrhenius plot for the optimized system of starch: 25 wt. % of  $\text{NH}_4\text{NO}_3$

Table 1 Conductivity and activation energy for starch: 25 wt. % of  $\text{NH}_4\text{NO}_3$

Glycine (wt. %)	$\sigma$ (S cm <sup>-1</sup> )	$E_a$ (eV)
0	$2.85 \pm 1.99 \times 10^{-5}$	-
2	$1.55 \pm 0.25 \times 10^{-5}$	0.40
4	$8.55 \pm 0.89 \times 10^{-5}$	0.28
6	$2.89 \pm 0.19 \times 10^{-5}$	0.47
8	$5.04 \pm 1.22 \times 10^{-6}$	0.59
10	$6.64 \pm 3.19 \times 10^{-6}$	0.54

The dielectric relaxation behavior of the polymer electrolyte brings important insights into the ionic transport phenomenon [7]. Fig. 4(a) and (b) represents the frequency dependence on dielectric constant at different concentrations of glycine and different temperatures for the highest conducting sample, respectively.

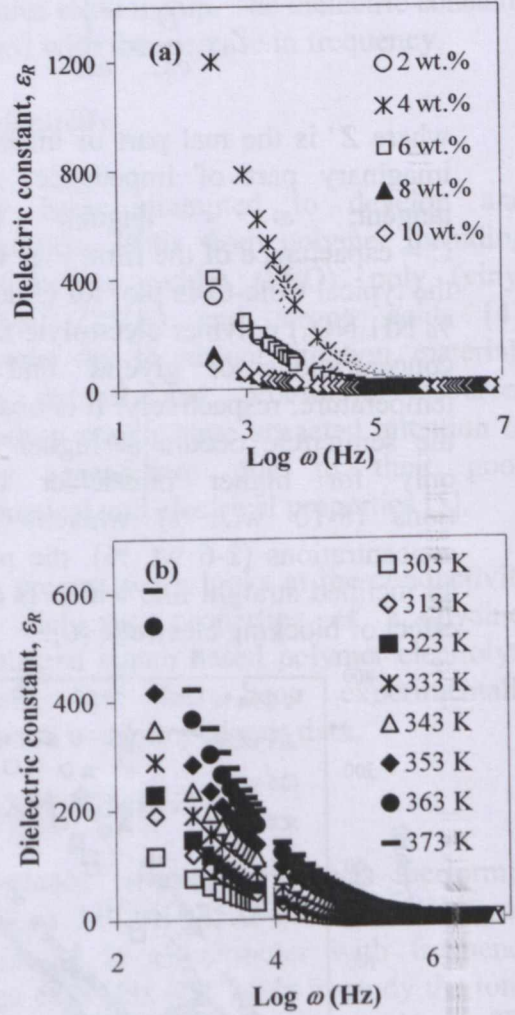
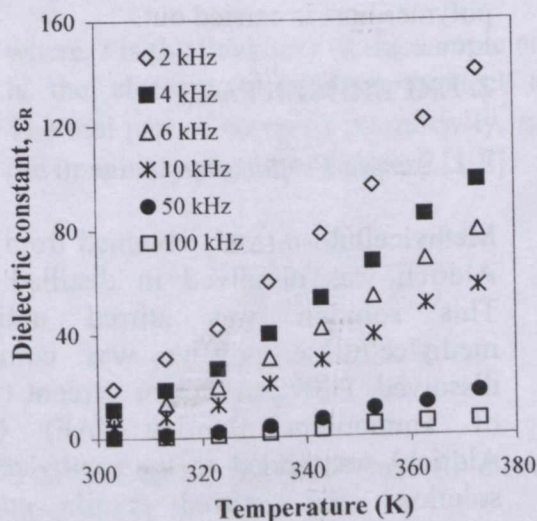


Fig. 4 Variation of dielectric constant at different frequencies for starch: 25 wt.% of  $\text{NH}_4\text{NO}_3$  at (a) different concentrations and (b) different temperatures



The figures clearly show a sharp rise at low frequency end indicating that electrode polarization and space charge effect has occurred. This confirms a non-Debye dependent of the system [8]. The low frequency dispersion is attributed to the charge accumulation at the electrode-electrolyte interface. While at the higher frequency, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field [9].

From Fig. 5, it is evident that the dielectric permittivity increases with increase in temperature. This variation is different in polar and non-polar materials where in the case of non-polar polymer the dielectric constant is independent of temperature but in the case on a polar polymer, the dielectric constant is dependent on the temperature [9]. The behavior observed in this plot is typical of polar dielectrics in which the orientation of dipoles is facilitated with the rising temperature and thereby the permittivity is increased [10].



**Fig. 5** Temperature dependence of dielectric constant at selected frequencies for starch: 25 wt. % of  $\text{NH}_4\text{NO}_3$ :4 wt. % glycine

#### 4. CONCLUSIONS

A plasticized system of starch: 25 wt. %  $\text{NH}_4\text{NO}_3$  was prepared using the solution casting technique. Analyses of impedance

data have determined the conductivity of the sample at different concentrations and temperature. The highest conductivity was obtained at  $8.55 \pm 0.89 \times 10^{-5} \text{ S cm}^{-1}$  for sample having 4 wt. % of glycine at 303 K. The temperature dependence data shows that sample exhibit Arrhenian behavior. The dielectric constant increased with the increase in temperature and decreased with the increase in frequency.

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